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BY

LAURENCE STANDLEY FOSTER

A.B. (Clark University) 1922
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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE DEPARTMENT OF BROWN UNIVERSITY, 1926

[Reprinted from Jour. Amer. Chem. Soc. 49, 457 (1927).]

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SOME PHENYLGERMANIUM DERIVATIVES

I. Introduction

For many years, tetra-ethylgermanium[1] has been the only known representative of the organic derivatives of germanium. Recently, Morgan and Drew[2] prepared tetraphenylgermanium and some of its derivatives, and Tabern, Orndorff and Dennis[3] prepared the same compound as well as a number of other quaternary organic germanium derivatives.

The chemistry of the organic germanium compounds is of particular interest since, in its chemical properties, germanium probably approaches carbon more nearly than does any other element. Comparing germanium with other elements of the fourth group, the properties of organic germanium compounds, for the most part, appear to lie intermediate between those of corresponding compounds of silicon and tin and approaching those of the former more nearly. The properties which particularly characterize carbon in its compounds are: (1) the stability of the carbon-to-carbon bond, (2) the stability of the carbon-hydrogen linkage and (3) the resistance of the carbon-halogen linkage towards hydrolysis.

With organic substituents attached to germanium, the germanium-to-germanium bond is much more stable than that of tin under corresponding conditions. Judging by the stability of the higher silicon hydrides, the silicon-to-silicon bond has the same order of stability as the germanium-to-germanium bond. With the exception of the triaryl methyls, the germanium-to-germanium bond is much less stable than the carbon-to-carbon bond. The stability of the germanium-hydrogen linkage is approximately the same as that of the silicon-hydrogen linkage and much greater than that of the tin-hydrogen linkage. The germanium-hydrogen linkage is much less stable than the carbon-hydrogen linkage with the possible exception of triphenylmethane.[4]

The germanium-hydrogen linkage is much less stable than the germanium-carbon linkage. Thus, the organic germanium hydrides of the

[1] Winkler, *J. prakt. Chem.*, **36**, 177 (1887).

[2] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

[3] Tabern, Orndorff and Dennis, *J. Am. Chem. Soc.*, **47**, 2039 (1925).

[4] Kraus and Rosen, *J. Am. Chem. Soc.*, **47**, 2739 (1925).

type R_nGeH_{4-n} are readily converted to the corresponding halides by direct halogenation or by the action of halogen-acids, the hydrogen atoms being substituted. Tetraphenylgermanium, on the other hand, is brominated with difficulty and substitution may be confined to a single phenyl group. This is in marked contrast to tetraphenyltin, in the case of which two phenyl groups are readily substituted by halogens, either directly or by the action of the corresponding acids. Toward strong reducing agents, such as sodium in liquid ammonia, tetraphenylgermanium and tetraphenyltin are about equally reactive.

The halogen-carbon linkage is ordinarily hydrolyzed with considerable difficulty. Corresponding compounds of germanium or silicon are readily hydrolyzed. On the other hand, the halogen-tin linkage is relatively stable towards hydrolysis. With ammonia in place of water, the halogen derivatives of organic germanium and silicon compounds are readily ammonolyzed, while the corresponding tin compounds are stable. In this respect, tin approaches carbon more closely than does either germanium or silicon. The ready ammonolysis of organic germanium halides renders difficult many convenient reactions readily carried out with corresponding tin compounds in liquid ammonia.

The purpose of the present investigation was to gain a general notion of the properties of various derivatives of triphenylgermanyl. Because of the high cost of germanium, methods for the preparation of source materials are described in sufficient detail to enable others to duplicate the results.

II. Tetraphenylgermane, $(C_6H_5)_4Ge$

Preparation.—This compound has been prepared by Morgan and Drew[2] and by Tabern, Orndorff and Dennis[3] by means of the Grignard reagent, but the yields obtained are not reported. The former investigators used germanium tetrabromide and the latter, germanium tetrachloride. In the present investigation, germanium tetrabromide was employed in preference to the chloride because of its lower volatility. A number of experiments with the Grignard reagent failed to give satisfactory yields. Accordingly, a method of preparation was adopted which is similar to that described by Chambers and Scherer[5] for the preparation of tetraphenyltin.

Fourteen and two-tenths g. of magnesium turnings was treated with 76.4 g. of bromobenzene in 200 cc. of absolute ether, and on completion of the reaction, the ether solution of the Grignard reagent was transferred, by means of nitrogen pressure, through a siphon tube into a 3-necked, round-bottomed flask. This flask was fitted with a reflux condenser, a drying tube, a funnel and a tube reaching to the bottom to permit stirring the reaction mixture by means of a stream of nitrogen. Thirty-three and two-tenths g. of anhydrous zinc chloride, previously dried over phosphorus pentoxide, was suspended in 100 cc. of ether and slowly introduced into the Grignard reagent. The reaction mix-

[5] Chambers and Scherer, *J. Am. Chem. Soc.*, **48**, 1054 (1926).

ture was kept cold under continued stirring for one hour, after which the mixture was boiled for an hour. One hundred cc. of dry toluene was then added and the ether was distilled on a water-bath. The flask was then cooled in ice water and 14.91 g. of germanium tetrabromide, dissolved in toluene, was slowly added while the mixture was stirred vigorously. After introducing the germanium tetrabromide, the contents of the flask were boiled on an oil-bath for 16 hours under an atmosphere of nitrogen. At the end of that time the toluene solution was only slightly colored.

The flask was then placed in an ice-bath and 200 cc. of 2 *N* sulfuric acid added to remove residual zinc and magnesium compounds. A great deal of heat was evolved in this process. The water-toluene mixture was then boiled until all solid material was dissolved. The toluene was separated from the water layer while still warm since, otherwise, a portion of the tetraphenylgermanium crystallized out. After separating and drying, the toluene was distilled and the last traces removed with a vacuum pump. The resulting product was recrystallized from benzene and finally washed with low-boiling petroleum ether. The crude material originally obtained was remarkably pure. Contrary to the observation of Morgan and Drew,[2] the color of the material in bulk was found to be white. The results of several preparations are given in Table I.

TABLE I

SUMMARY OF YIELDS IN THE PREPARATION OF TETRAPHENYLGERMANE

$GeBr_4$, g.	$Ge(C_6H_5)_4$, g.	Yield		Boiled, hrs.
		Calcd., g.	Obtained, %	
7.27	5.17	7.04	73.2	1
6.00	4.80	5.82	82.4	2
6.45	5.71	6.26	90.7	6
12.61	10.16	12.24	83.0	2.5
14.91	13.78	14.46	95.4	16
20.71	18.68	20.09	92.9	16

As may be seen from Table I, excellent yields were obtained when the reaction mixture was boiled sufficiently.

Properties.—The melting point of a carefully purified sample of tetraphenylgermane, as determined by means of a thermocouple in a specially designed apparatus, was found to be 235.7°, which is markedly higher than the values recorded in the literature.

Tetraphenylgermane is readily soluble in hot benzene and toluene, the solubility diminishing greatly with the temperature. It is readily soluble in chloroform, moderately soluble in carbon tetrachloride, carbon disulfide and acetone and slightly soluble in alcohol, ether and petroleum ether.

Metallic sodium in liquid ammonia reacts slowly with tetraphenylgermane to form sodium triphenyl germanide, $NaGe(C_6H_5)_3$, sodium amide and benzene, the reaction resembling that between sodium and tetramethyltin.[6] The slowness of the reaction may be due to the low solubility of the germane in liquid ammonia. When concentrated sodium solutions are used, a second phenyl group is substituted as was indicated by the characteristic red color of the solution formed. With respect to reduction by metallic sodium, tetraphenylgermane closely resembles tetraphenylstannane.[5]

III. Triphenylgermanium Bromide, $(C_6H_5)_3GeBr$

Preparation.—This compound has been prepared by Morgan and Drew[2] by means of the Grignard reagent. It is readily obtained in prac-

[6] Kraus and Sessions, *J. Am. Chem. Soc.*, **47**, 2361 (1925).

tically quantitative yield by the direct bromination of tetraphenylgermane in boiling carbon tetrachloride.

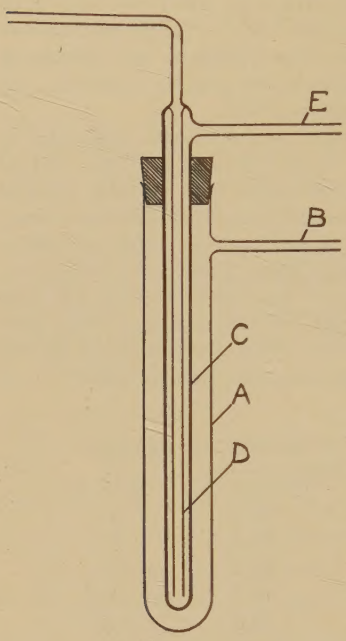

Fig. 1.

Tetraphenylgermane and bromine (in slight excess) are introduced into about five times their weight of pure carbon tetrachloride contained in a round-bottomed flask which is provided with a reflux condenser sealed directly to it. The mixture is boiled for seven hours, at the end of which time the reaction is practically complete. The carbon tetrachloride and excess of bromine are distilled and the last traces removed with a vacuum pump.

Final purification of the product is effected by distillation in a high vacuum at 150°, at which temperature tetraphenylgermane is not appreciably volatile. Distillation was carried out in an apparatus outlined in the accompanying figure. The raw material is placed in the bottom of Tube *A* which in turn is placed in a Crisco-bath at the desired temperature. A high-vacuum pump is attached at *B*. *C* is a condenser through which a stream of cold water is kept flowing. The end of the condenser is placed a few centimeters above the level of the material in the bottom of Tube *A*. The triphenylgermanium bromide, which condenses on the end of the condenser *C* in the form of a solid mass, is removed from time to time until separation is completed. Even with a comparatively impure product, at most, two distillations are required.

Properties.—Triphenylgermanium bromide is very soluble in ordinary organic solvents such as chloroform, carbon tetrachloride, benzene and toluene. It is less soluble in alcohol and only slightly soluble in petroleum ether. The latter solvent affords the best means for recrystallization. The melting point, as determined by means of a thermocouple, was found to be 138.7°.

Reactions.—As Morgan and Drew have shown, triphenylgermanium bromide hydrolyzes slowly in water and more readily in the presence of alkalies. The product of hydrolysis, however, is not the hydroxide, but the oxide, $[(C_6H_5)_3Ge]_2O$. The bromide is readily soluble in liquid ammonia but is largely ammonolyzed and on evaporation of the solvent, tri-triphenylgermanylamine, $[(C_6H_5)_3Ge]_3N$, is obtained.[7]

IV. Hexaphenylgermano-ethane, $[(C_6H_5)_3Ge]_2$

Preparation.—Hexaphenylgermano-ethane, or triphenylgermanyl, was prepared according to the method of Morgan and Drew[2] by the reduction of triphenylgermanium bromide with metallic sodium in boiling xylene. In carrying out this reduction, oxygen must be excluded rigidly. On cooling, fine white crystals separated. This product was heated to about

[7] Observations of Mr. Charles B. Wooster in this Laboratory, to be published later.

200° in a high vacuum to remove traces of triphenylgermanium bromide, and the residue was recrystallized from benzene.

Properties.—Hexaphenylgermano-ethane is only slightly soluble in ordinary organic solvents and is almost insoluble in liquid ammonia. Apparently, the bond between the germanium atoms in this compound is a very stable one. On treating a suspension of this material with sodium in liquid ammonia, reaction takes place somewhat slowly with the formation of sodium triphenyl germanide, $NaGe(C_6H_5)_3$. It may be brominated to triphenylgermanium bromide in boiling carbon tetrachloride. The rate of bromination is approximately the same as that of tetraphenylgermane. This behavior of hexaphenylgermano-ethane is in striking contrast to that of the corresponding tin compound, in the case of which bromination takes place almost instantaneously.

V. Triphenylgermanium Fluoride, $(C_6H_5)_3GeF$

Preparation.—Triphenylgermanium oxide, prepared according to the method of Morgan and Drew, was heated with hydrofluoric acid in a platinum dish. When the solid oxide had disappeared, the excess of hydrofluoric acid was evaporated, leaving behind the triphenylgermanium fluoride as a liquid which solidified on cooling. It was purified by distillation in a vacuum at 150°, as described in the case of the bromide. The yield is practically quantitative. The compound was analyzed for fluorine by the method of Starck.[8] The fluoride was hydrolyzed in a boiling solution of dil. sodium hydroxide, the oxide (m. p., 182°) was separated by filtration and the fluorine precipitated from the filtrate as lead chlorofluoride and weighed as such.

Anal. Subs., 0.2430, 0.2548: PbClF, 0.1929, 0.1999. Calcd. for $(C_6H_5)_3GeF$: F, 5.89. Found: 5.76, 5.69.

Properties.—Triphenylgermanium fluoride melts at 76.6° (corr.). It is insoluble in water and practically insoluble in liquid ammonia. In organic solvents, the fluoride is extremely soluble, much more so than the other triphenylgermanium halides. It is best recrystallized from low-boiling petroleum ether, in which it is readily soluble.

Reactions.—Like the bromide, the fluoride is hydrolyzed by alkalies, but much less readily. On boiling with potassium hydroxide in absolute alcohol for 15 minutes, no reaction occurs. The fluoride is less readily ammonolyzed than the corresponding bromide. On treating sodium triphenyl germanide with triphenylgermanium fluoride, an appreciable quantity of hexaphenylgermano-ethane was obtained. On passing ammonia gas through a solution of triphenylgermanium fluoride in petroleum ether, precipitation of ammonium fluoride occurred only at the end of about ten minutes; in the case of the bromide, precipitation occurs immediately. The fluoride is thus the most stable of the triphenylgermanium halides.

VI. Triphenylgermanium Iodide, $(C_6H_5)_3GeI$

This compound was prepared by agitating a chloroform solution of triphenylgermanium oxide with an aqueous solution of hydriodic acid. The resulting chloroform

[8] Starck, *Z. anorg. Chem.*, **70**, 173 (1911). Compare Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926).

solution of the iodide exhibited a pink color, owing to the presence of free iodine. After being dried, the chloroform solution was decolorized by means of finely divided silver, after which it was evaporated to dryness under reduced pressure. The resulting product was recrystallized from low-boiling petroleum ether. The crystals so obtained were pure white but acquired a yellowish tint after exposure to air for a few minutes; m. p., 157° (corr.).

Anal. Subs., 0.2350, 0.2630: AgI, 0.1260, 0.1389. Calcd. for $(C_6H_5)_3GeI$: I, 29.47. Found: 28.97, 28.50.

Triphenylgermanium iodide is very unstable. It hydrolyzes readily and its solutions in petroleum ether acquire a pink color, due to free iodine, after standing exposed to the atmosphere for only a short time.

VII. Sodium Triphenyl Germanide, $(C_6H_5)_3GeNa$

Preparation.—Sodium triphenyl germanide is prepared by treating hexaphenylgermano-ethane with an equivalent quantity of sodium in liquid ammonia solution. The reaction takes place somewhat slowly, probably because of the low solubility of the germano-ethane. The concentration of sodium must not be too high as, otherwise, phenyl groups are substituted by the metal.

Two atoms of sodium react with 1 mole of hexaphenylgermano-ethane according to the equation

$$2\,Na + [(C_6H_5)_3Ge]_2 = 2\,NaGe(C_6H_5)_3 \qquad (1)$$

In Table II are given the results of a number of experiments in which the weights of the reacting materials and their products were determined.

Small pieces of sodium cut under oil and handled in the absence of air were introduced into the reaction tube until the blue color, due to free sodium, became permanent. The color reaction is very sensitive and the precision of the results is determined by the size of the bits of sodium introduced. The amount of sodium actually added to give a permanent blue color is given in Col. 2 and the amount required according to Equation 1, in Col. 3. As may be seen from the table, the results are in excellent agreement with Equation 1.

TABLE II

SUMMARY OF RESULTS IN THE REACTION OF SODIUM WITH HEXAPHENYLGERMANO-ETHANE

$Ge(C_6H_5)_6$, g.	Na added, g.	Na required, g.
0.8150	0.0620	0.0617
1.1020	.0859	.0835
1.0747	.0816	.0814
0.4953	.0363	.0375
1.9773	.1504	.1498
1.9927	.1519	.1509

Properties.—Sodium triphenyl germanide is exceedingly soluble in liquid ammonia. Dilute solutions are colored faintly yellow, while concentrated solutions exhibit an orange color. The concentrated solutions are extremely viscous.

The crystals obtained from liquid ammonia solution contain 3 moles of ammonia which are lost fairly readily at lower pressures. The results of a number of determinations of the ammonia content are given in Table III.

TABLE III

AMMONIA OF CRYSTALLIZATION IN SODIUM TRIPHENYL GERMANIDE

$NaGe(C_6H_5)_3$, g.	NH_3 found g.	NH_3, moles
0.8767	0.1295	2.87
1.1855	.1839	2.81
0.9058	.1400	2.95

Sodium triphenyl germanide is fairly soluble in ether and pure benzene. It is very soluble in benzene saturated with ammonia. Solutions of triphenyl germanide in liquid ammonia are as highly ionized as are ordinary salts, and its solutions in benzene in the presence of ammonia conduct the current with considerable facility.[9]

Reactions.—Sodium triphenyl germanide is extremely reactive toward electronegative elements or compounds containing such elements. This was to have been expected since the triphenyl germanide anion is only weakly electronegative. In the presence of electronegative elements, or non-ionic compounds of such elements, the germanide ion loses its electron to the negative element. The sodium, or any other strongly positive element, plays no direct part in such reactions; it merely supplies the balancing electrical charge.

Sodium triphenyl germanide is readily oxidized to the germanolate, $(C_6H_5)_3GeONa$. With ammonium bromide, or with water, it yields triphenylgermane, $(C_6H_5)_3GeH$, quantitatively. With triphenylgermanium fluoride in liquid ammonia, a small quantity of hexaphenylgermano-ethane is obtained. On treating an ethereal solution of sodium triphenyl germanide with phenyl bromide, the chief product is tetraphenylgermane. However, about 10% of the material was recovered in the form of hexaphenylgermano-ethane. With trimethyltin bromide, the chief product of reaction is trimethylstannyl-triphenylgermane, $(CH_3)_3Sn.Ge(C_6H_5)_3$. Hexaphenylgermano-ethane and hexamethylstanno-ethane are likewise formed in small amounts.

VIII. Sodium Triphenyl Germanolate, $(C_6H_5)_3GeONa$

Preparation.—This compound was prepared by oxidizing sodium triphenyl germanide in liquid ammonia. The same compound is obtained by carrying out the oxidation in the dry state or in benzene. In Table IV are given data relating to the oxidation of sodium triphenyl germanide in liquid ammonia.

In Col. 2 are given the volumes of oxygen absorbed and in Col. 3 the weights as found from the increase in weight of the contents of the reaction tube.

[9] Data relative to the conductance of sodium triphenyl germanide in various solvents will appear in a subsequent paper.

TABLE IV

OXIDATION OF SODIUM TRIPHENYL GERMANIDE

$NaGe(C_6H_5)_3$, g.	O_2 abs., cc.	O_2 calcd., cc.	O_2 abs., g.	O_2 calcd., g.
1.1785	43.6	40.7	0.0576	0.0580
0.9120	..	..	.0447	.0446

As may be seen from Table IV, the volume of oxygen absorbed and, more particularly, the weight of the reaction product corresponds closely with that required (Cols. 3 and 5) for the reaction

$$NaGe(C_6H_5)_3 + {}^1/_2\, O_2 = NaOGe(C_6H_5)_3 \qquad (2)$$

Properties.—Sodium triphenyl germanolate is practically insoluble in liquid ammonia. It is extremely soluble in benzene and readily soluble in petroleum ether. The product from petroleum ether melts at approximately 100° but the dry product from liquid ammonia failed to melt up to 250°. Presumably, the compound separating from petroleum ether contains solvent of crystallization.

The compound obtained from liquid ammonia contains one molecule of the solvent as indicated by the following data.

Anal. Subs., 1.2231: NH_3, 0.0480. Calcd. for $NH_3.NaOGe(C_6H_5)_3$: NH_3, 0.0475 g.

The benzene solution of sodium triphenyl germanolate exhibits an orange color. In liquid ammonia, sodium triphenyl germanolate reacts readily with ammonium bromide to form the corresponding germanol and the same product is obtained on treating a benzene solution of the germanolate with water. The products of hydrolysis of the germanolate serve to establish the constitution of that compound.

IX. Triphenyl Germanol, $(C_6H_5)_3GeOH$

Preparation.—It might be expected that this compound would be formed on hydrolyzing the corresponding halides in water or alkaline solution. Morgan and Drew, however, failed to obtain triphenyl germanol in this way. Our own observations confirm those of Morgan and Drew. The compound is best prepared by treating a benzene solution of sodium triphenyl germanolate with water. The product may conveniently be recrystallized from petroleum ether.

Anal. Subs., 0.1949, 0.2352: GeO_2, 0.0634, 0.0761. Calcd. for $(C_6H_5)_3GeOH$: Ge, 22.64. Found: 22.58, 22.45.

Mol. wt. (cryoscopic method). Subs., 0.1287, 0.2609 in C_6H_6, 12.345, 12.345: Δt, 0.154, 0.294°. Calcd. for $(C_6H_5)_3GeOH$: mol. wt., 320.6. Found: 358, 359.

The high value of the molecular weight may be due to the presence of oxide.

Properties.—The solubility of triphenyl germanol in organic solvents is about the same as that of triphenylgermanium bromide. From petroleum ether it crystallizes in the pure state while from benzene it crystallizes with solvent of crystallization. It melts at 134.2° (corr.) without appreciable loss of water. At temperatures much above the melting point, water is lost slowly. On heating a quantity of the germanol to 200° in an evacuated inverted U-tube, the second limb of which was immersed in boiling ammonia, crystals of ice were obtained. The melting point of the product remaining in the first limb rose from 130° to 170° at the end of two hours. The melting point of triphenylgermanium oxide is 184°.

X. Triphenylgermane, $(C_6H_5)_3GeH$

Preparation.—This compound is prepared quantitatively by treating sodium triphenyl germanide with ammonium bromide in liquid ammonia or by treating a benzene solution of the same compound with water. After evaporation of the ammonia, the germane is extracted from the residue with petroleum ether. The ether is evaporated at ordinary temperatures under reduced pressure. The viscous liquid thus obtained crystallizes on cooling in ice water. The product is purified by distilling in a vacuum at a pressure of 0.01 mm. and a temperature of 150°. Under these conditions, clear drops of oily liquid are collected which freeze to a white solid.

Anal. Subs., 0.2711, 0.3316, 0.2762: GeO_2, 0.0929, 0.1136, 0.0946. Calcd. for $Ge(C_6H_5)_3H$: Ge, 23.83. Found: 23.78, 23.77, 23.77.

Mol. wt. (cryoscopic method). Subs., 0.1466, 0.3556; in C_6H_6, 17.789, 17.789: Δt, 0.139, 0.327°. Calcd. for $Ge(C_6H_5)_3H$: mol. wt., 304.6. Found: 300.4, 305.6.

Properties.—Triphenylgermane exists in two monotropic forms. The more stable form, α, melts at 47° and the less stable, β, at 27°. The melt of the β form, maintained at 30°, freezes immediately and completely when seeded with the α form.

Triphenylgermane is extremely soluble in such solvents as benzene, toluene, chloroform and petroleum ether and very soluble in ether and carbon tetrachloride. It is fairly soluble in methyl alcohol, from which it is precipitated on addition of water. It is slightly soluble in liquid ammonia. Triphenylgermane shows no sign of decomposition at 250°. Its hot vapors are extremely penetrating and irritating.

Reactions.—Under ordinary conditions, triphenylgermane is stable in air but on very long standing there are indications that oxidation occurs. It reacts immediately with the halogens to form triphenylgermanium halides, and the same compounds are formed on treating it with strong halogen acids.

Triphenylgermane is readily reduced by sodium in liquid ammonia solution, sodium triphenyl germanide being formed and hydrogen evolved. The reaction, however, does not proceed quantitatively. The amount of hydrogen obtained is always less than that corresponding to the equation

$$(C_6H_5)_3GeH + Na = NaGe(C_6H_5)_3 + {}^1/_2\,H_2 \qquad (3)$$

The solution, on completion of the reaction, was always found to be tinged with red, indicating the presence of disodium diphenyl germanide. On treating this solution with ammonium bromide, a mushy precipitate was obtained, showing the presence of a substance that was liquid at liquid ammonia temperature. These facts indicate the presence of diphenylgermane. Following are data relating to the amount of gas evolved.

$Ge(C_6H_5)_3H$, 0.8950, 0.8867, 0.9896: H_2, 27.0, 20.6, 28.5 cc. Calcd. (Equation 3): 32.9, 32.6, 36.4 cc. Yield, 81.8, 63.0, 79.0%.

The density of the evolved gas corresponded to a mean molecular weight of 3.1, showing that it was chiefly hydrogen.

XI. Trimethylstannyl-triphenylgermane, $(CH_3)_3Sn.Ge(C_6H_5)_3$

Preparation.—This compound is readily prepared by treating an ammonia solution of sodium triphenyl germanide with trimethyltin bromide. Reaction takes place immediately with the formation of a solid precipitate. The material is extracted from

the reaction mixture with petroleum ether and the solution concentrated in a flask under reduced pressure at room temperature. The crystals separating out under these conditions appear to be quite pure, since they melt sharply.

Anal. Subs., 0.1668, 0.2497: $GeO_2 + SnO_2$, 0.1014, 0.1342. Calcd. for $(CH_3)_3Sn{\cdot}Ge(C_6H_5)_3$: 0.1020, 0.1363 g.

Mol. wt. (cryoscopic method). Subs., 0.0825, 0.1807; in C_6H_6, 18.01, 18.01: Δt, 0.058, 0.123°. Calcd. for $(CH_3)_3Sn.Ge(C_6H_5)_3$: mol. wt., 467.1. Found: 394.8, 407.7.

The values found for the molecular weight are somewhat low, probably owing to the presence of impurities and the small temperature change obtained. The compound was found to melt sharply at 88°.

Properties.—Trimethylstannyl-triphenylgermane is a white, crystalline solid with a slight odor characteristic of organic tin compounds. It is very soluble in carbon tetrachloride, benzene, chloroform and petroleum ether. In the last-named solvent, the solubility diminishes considerably with falling temperature, for which reason it serves as a convenient recrystallizing medium. It is somewhat soluble in alcohol from which it is precipitated on adding water.

It reacts readily and quantitatively with bromine to form a mixture of triphenylgermanium and trimethyltin bromides, respectively. Apparently it does not dissociate, even in boiling benzene, since oxygen passed through such a solution for several hours gives no evidence of the precipitation of trimethyltin oxide, nor is the melting point of the material changed thereby.

The authors gratefully acknowledge their indebtedness to the New Jersey Zinc Company for a quantity of germanium oxide, with which material the present investigation was initiated.

Summary

1. The chemistry of organic germanium derivatives is compared with that of other elements of the fourth group.

2. Methods are described for the preparation of tetraphenylgermanium and triphenylgermanium bromide.

3. Triphenylgermanium fluoride, triphenylgermanium iodide, sodium triphenyl germanide, sodium triphenyl germanolate, triphenyl germanol, triphenylgermane and trimethylstannyl-triphenylgermane have been prepared and some of their properties and reactions have been studied.

4. Germanium compounds are much more stable toward oxidizing agents than are the corresponding tin compounds, but toward strong reducing agents their behavior is very similar to that of the latter. The triphenylgermanium halides hydrolyze and ammonolyze much more readily than do the corresponding halides of tin.